

Spectral properties of Tb(III) and Nd(III) complexes with 3,3'-[(phenylmethylene)]bis(4-hydroxy-2H-1-benzopyran-2-one)

V. KIRCHEVA^{a,*}, J. ZAHARIEVA^a, I. MANOLOV^b, M. MILANOVA^a

^aSofia University, Faculty of Chemistry, Department of Inorganic Chemistry, 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria,

^bMedical University, Faculty of Pharmacy, Department of Organic Chemistry, 1, Dunav Str., 1000 Sofia, Bulgaria

Complexes of the trivalent lanthanoid ions of Nd(III) and Tb(III) with some 3,3'-[(phenylmethylene)]bis(4-hydroxy-2H-1-benzopyran-2-one) derivatives such as 3,3'-[(4-chlorophenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) and 3,3'-[(3,5-dimethoxy-4-hydroxyphenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) were synthesized, following three synthetic procedures. The complexes formed were investigated with elemental analysis, IR- spectroscopy, and fluorescence spectroscopy. Deconvolution of IR-spectra was applied and used to elucidate the molecular structure and the possibilities for coordination of coumarin ligands to the lanthanoid (III) ions. Based on the vibrational analysis coordination through deprotonated hydroxyl group and oxygen atom of the carbonyl group is suggested. Excitation and emission spectra of the newly synthesized complexes were recorded and interpreted. The water molecules coordinated do not influence the emission in the visible region of the Tb(III) complexes while in the case of Nd(III) complex they perform as a very strong quenching agent. The Nd(III) complexes without any coordinated water molecules but with acetonitrile in the outer sphere show the intensive band at 1050 nm responding to the strongest transition $^4F_{3/2} \rightarrow ^4I_{11/2}$.

(Received August 10, 2020; accepted October 7, 2021)

Keywords: 3,3'-[(phenylmethylene)]bis(4-hydroxy-2H-1-benzopyran-2-one) derivatives, Tb complexes, Nd complexes, Fluorescence

1. Introduction

The coordination compounds containing trivalent lanthanoids with luminescent properties have attracted attention in last decades because of their application in the performance of different devices. The lanthanoid complexes have been used in fluorometric determination, for instance of coumarins [1]. Some of the coumarins give a low analytical signal and therefore a high detection limit for fluorometry. The sensitivity of the fluorometric determination can be enhanced by the formation of complexes, i.e. by using the so-called sensitized fluorescence [1]. Lanthanoid complexes have been used both in electroluminescent devices, ultraviolet dosimeters and fluorescent labels [2], and molecular biology [3].

In view of the spectral properties of the lanthanoid ions the intraconfigurational 4f–4f transitions should be considered. They are parity forbidden (Laporte rule) so consequently the absorption and emission spectra of the lanthanoid ions show weak intensity. Among the others, the Tb(III) ion has a low molar absorptivity, so direct excitation of the Tb(III) luminescence is difficult unless laser excitation is used or high concentration of the ion ($> 10^{-2}$ M). However, the population of the excited states of the Ln(III) ions may be increased by coordination to organic ligands, which act as sensitizers. Terbium luminescence can be sensitized by energy transfer from ligands as ketones or aromatic moieties. In Ln(III) complexes the organic ligands absorb and transfer energy efficiently to the metal ion (intramolecular energy transfer) and consequently increase their luminescence intensity. One of the many potential advantages of Ln(III) ions for applications is the narrow

bands displayed by the emission spectra of Ln complexes due to the effective shield of the $4f^N$ orbitals from the influence of the chemical environment by the 5s5p orbitals [4]. To exploit the lanthanoid advantages different complexes have been synthesized [5-7]. Among them, complexes with different coumarin derivatives within the recent years have shown promising properties and because of that they have attracted a lot of interest [8-12].

In our group some complexes of bis-coumarin derivatives with lanthanoids were synthesized. Among them the complex of 3,3'-[(4-chlorophenyl)methylene] bis(4-hydroxy-2H-1-benzopyran-2-one) with Nd(III) of the type $Nd_2L_3 \cdot 4H_2O$ (NdL15) with metal : ligand ratio = 2:3 was prepared and molecular structure was proposed based on IR-spectroscopy and literature data [13]. In an attempt to diminish the influence of water molecules a water-free synthetic procedure with an aprotic solvent was applied; a complex of 3,3'-[(3,5-dimethoxy-4-hydroxyphenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) with Nd(III), mentioned in [13], with Nd(III) to ligand mole ratio 1:1, of the type $[NdL(NO_3)_3] \cdot 2CH_3CN$, was obtained. These complexes contained within in [13] were only partly investigated.

The work presented here is a continuation and development of the investigations started some time ago that is why the first part of the results and discussion is connected with the previous research, mainly the results from IR spectroscopy. The essential improvement is to prove the nature of the water molecules in IR spectra in order to follow their influence on the optical properties. As this will be seen, the presence of the water molecules can

be significant considering especially the fluorescence properties of the complexes.

The work is an attempt to elucidate and underline the role of the structure on the optical properties of the complexes and to extend the knowledge for coordination of coumarin-ligands with lanthanoid ions. In the text only two lanthanoids Ln(III) are experimented, Nd(III) from the light lanthanoids and Tb(III) from the middle of the lanthanoids. As ligands the already mentioned two bis-coumarin derivatives of 3,3'-[(phenylmethylene)]bis(4-hydroxy-2H-1-benzopyran-2-one) are used, specifically 3,3'-[(4-chlorophenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) (with a symbol L15) and 3,3'-[(3,5-dimethoxy-4-hydroxyphenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) (with a symbol L11).

2. Experimental

2.1. Materials and methods used

The ligands 3,3'-[(4-chlorophenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one), $C_{25}H_{15}O_6Cl$ (L15) and 3,3'-[(3,5-dimethoxy-4-hydroxyphenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one), $C_{27}H_{20}O_9$ (L11) used in this study were prepared by Manolov and colleagues, following the synthetic procedure presented in [14]. The Fig. 1 gives the structure of the ligands.

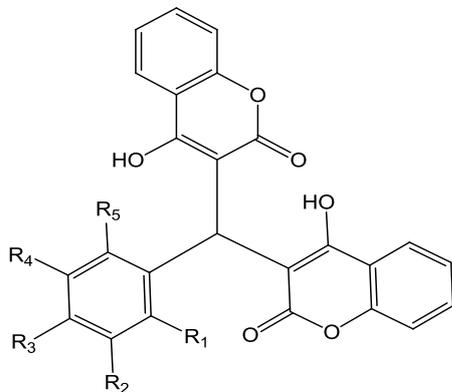


Fig. 1. The ligands L15, where $R_1=H$, $R_2=H$, $R_3=Cl$, $R_4=H$, $R_5=H$ and L11, $R_1=H$, $R_2=OCH_3$, $R_3=OH$, $R_4=OCH_3$, $R_5=H$

The metal salts used were the lanthanoid nitrates, among them $Nd(NO_3)_3 \cdot 6H_2O$, p.a. grade, Fluka. $Tb(NO_3)_3 \cdot 6H_2O$ was synthesized from Tb_4O_7 , p.a., Fluka. Tetraethylammonium hydroxide, Et_4NOH , (Sigma-Aldrich) as 40% water solution was utilized. All other solvents and reagents used were of analytical grades. The details of the synthetic procedures for complexes preparation are presented below.

Elemental analysis for carbon, hydrogen, nitrogen is performed according to standard analytical procedures with Vario EL III. The content of lanthanoids (neodymium and terbium) and water was determined by complexometric titration with solution of Complexon III at a value of pH 6 (acetate buffer) with indicator xylenol orange.

The infrared spectra were obtained with Nicolet 6700 and Bomem Michelson 100 spectrophotometers. The spectra are made in nujol suspension at splitting capacity ± 2 cm^{-1} and accumulation of 50 scans. To work on the data a program Spectra Calc was used for deconvolution of the spectral curves.

The recording of the excitation and the emission spectra of the ligands and the respective complexes were done by a fluorescent spectrometer Cary Eclipse (Varian) assembled with Hg lamp.

A fluorescent microscope N-400 M was used to observe the fluorescent green light emission from the Tb(III) powdered samples for evaluation of sample homogeneity.

2.2. Preparation of the complexes

All the complexes were synthesized during the reaction between lanthanoid nitrate and the ligand, following three synthetic routes. The later ones are presented briefly in the scheme in Fig. 2 as well as in details below one after another.

The first synthetic route, also applied in [13], is utilizing a deprotonation of the OH-groups of the ligand by a diluted water solution of NaOH. By that a sodium salt of the ligand in a water solution is obtained. To the solution mentioned a water solution of the Ln(III) nitrate is added in a metal to ligand mole ratio 2:3. This approach is a very simple one but the easy hydrolysis of the Na salt of the ligand requires rapid handling. Otherwise the ligand partially formed after the hydrolysis can mix to the complex and later causing a difficulty with the purification.

The second synthetic route, as simple as the first one, is applied for deprotonation of the OH-groups of the ligand, using 40 wt. % stable water solution of tetraethylammonium hydroxide, Et_4NOH , $[(C_2H_5)_4N]OH$; a tetraethylammonium salt of the ligand is formed, which is stable with the time. An ethanol solution of the Ln(III) nitrate is added to form the complex.

In all cases stirring with an electromagnetic stirrer for 3-4 h at room temperature was applied. The suspension formed was colored according to the color of the lanthanoid nitrate used. Then the suspension was filtered, washed thoroughly with water and dried in a desiccator with silica gel to constant weight.

The third synthetic route applied is excluding a deprotonation of the ligands by dissolving them in the aprotic solvent acetonitrile. It means that a positively charged complex can be formed when the ethanol solution of the Ln(III) nitrate is added in a metal to ligand mole ratio 1:2. The molar ratio metal to ligand depends on the complex to be obtained. In this case the complex formed had a high solubility in acetonitrile, so for its isolation the solution was concentrated slowly at temperature $50^\circ C$ without boiling.

The complexes synthesized by the synthetic routes mentioned above are amorphous, stable at room temperature, practically insoluble in common organic solvents but very soluble in DMSO. The results from the elemental analysis for C, H, N and Ln(III) are presented below along with the stoichiometry of the complexes

proposed on that base. The symbols of the complexes are given in parentheses showing the ligand used and the Ln(III) ion.

$\text{Nd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$ (NdL15): calc./found %C (53.15/53.02); %H (2.79/3.38); %Nd (17.02/18.13)

$\text{Tb}_2\text{L}_3 \cdot 2\text{H}_2\text{O}$ (TbL15): calc./found %C (53.35/53.65); %H (2.56/3.05); %Tb (18.82/18.84)

$\text{Tb}_2\text{L}_3 \cdot 12\text{H}_2\text{O}$ (TbL15-Et): calc./found %C (48.18/47.99); %H (3.39/3.26); %Tb (17.01/17.37)

$\text{Nd}_2\text{L}_3 \cdot 12\text{H}_2\text{O}$ (NdL11): calc./found %C (49.53/40.15); %H (4.00/3.88); %Nd (14.66/15.51)

$[\text{NdL}_2(\text{NO}_3)_3] \cdot 2\text{CH}_3\text{CN}$ (NdL11-AN2): calc./found %C (50.16/51.12); %H (3.33/3.24); %N (2.20/1.70); %Nd (10.39/10.70)

As can be seen from the results deviations for the carbon content are observed for one of the complexes. A possible reason could be the formation of stable lanthanide carbides and oxocarbonates during the analyses, which are not detected by the method used. This statement is made, based on a comparison of experimental results of analyses of our similar bis-coumarin complexes, carried out in two independent laboratories [15].

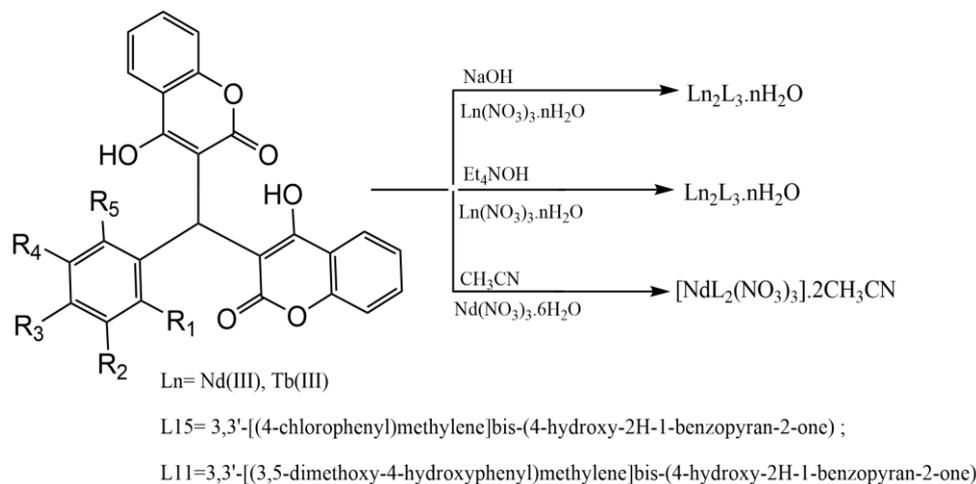


Fig. 2. Scheme of the three synthetic routes applied for synthesis of Ln(III) complexes with the coumarin ligands

3. Results and discussion

3.1. IR spectra of the ligands and the complexes

All the efforts for obtaining single crystals of the complexes turned out to be unsuccessful. Because of that, vibrational analysis was used to reveal the mode of coordination. The interpretation of IR spectral data was made by a comparison of the ligand spectra (L15 or L11) and the corresponding complexes as well as our previous research [13] and some literature data [16]. Following the first two synthetic procedures the ligands are deprotonated and the dianionic form obtained react with the Ln(III) ions. For similar bis-coumarins derivatives coordination of the ligands to Ln(III) ions through both the carbonylic oxygen atoms and the hydroxylic oxygen of the ligand was proposed [13, 16-17].

Some interpretation of IR spectra for similar complexes were already discussed and published [13]. Both the presence of water molecules, coordination through carbonylic and hydroxylic oxygen atoms were proposed [13, 16]. Detailed investigation of the IR spectra of L15 and NdL15 presented here is not only to prove complex formation but to elucidate the nature of water molecules presented in the complex. IR spectral data for L11 and its complexes NdL11 and NdL11-AN2 were also recorded. As long as the complexes were obtained by two different procedures the difference in their composition and spectral behavior is discussed below.

3.1.1. IR spectra of L15 and NdL15

In order to comment the presence and the nature of the water molecules, the IR spectra in the interval 3700-2600 cm^{-1} of the ligand L15 and NdL15 were analyzed (Fig. 3). The bands of the nujol at 1465 cm^{-1} and 1380 cm^{-1} are eliminated by subtraction of the IR spectrum of the pure nujol itself. A complete compensation of the absorption maxima between 3000-2800 cm^{-1} is not possible so the leftover bands are marked on each figure.

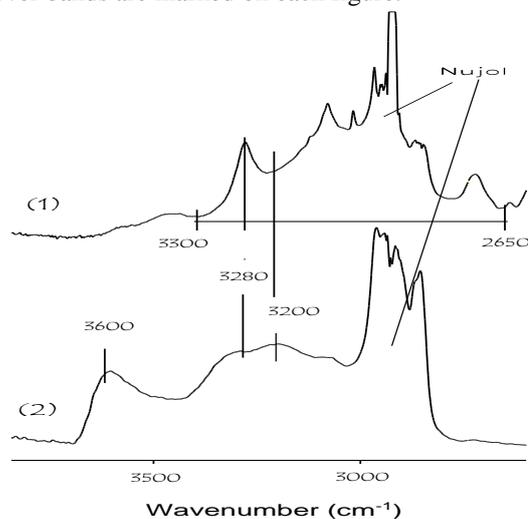


Fig. 3. IR spectrum of L15 (1, up) and NdL15 (2, down) in the interval 3700-2600 cm^{-1}

The leftover peaks both for nujol and for the stretching bands for the aromatic C-H bonds ($3100-3000\text{ cm}^{-1}$) are not considered. The multiplet band structure at $3200-2650\text{ cm}^{-1}$ can be assigned to strong intermolecular H-bonds in solid state, discussed as well in [12] and in [10]. The absorption maximum with small FWHM at 3280 cm^{-1} is probably due to intramolecular H-bond among the spatially closed OH-groups. The $1700-1350\text{ cm}^{-1}$ region of the ligand and the complex was briefly discussed in a previous our work [13]. More attention to the interval mentioned was paid applying spectral curve decomposition. According to Fig. 4 the sample contains negligible amount of unreacted ligand resulting in the band at 1660 cm^{-1} . The complexation leads to appearance of the intensive, with big FWHM, doublet at 1535 cm^{-1} and 1505 cm^{-1} in accordance with [13,17]. The band at 1625 cm^{-1} is assigned to bending vibrations of water molecules (not hydroxyl groups) [18]. The term crystal water in this case should be used to point out water molecules included in the inner coordination sphere of the complex. The specifying is needed because of the amorphous structure of the complexes presented.

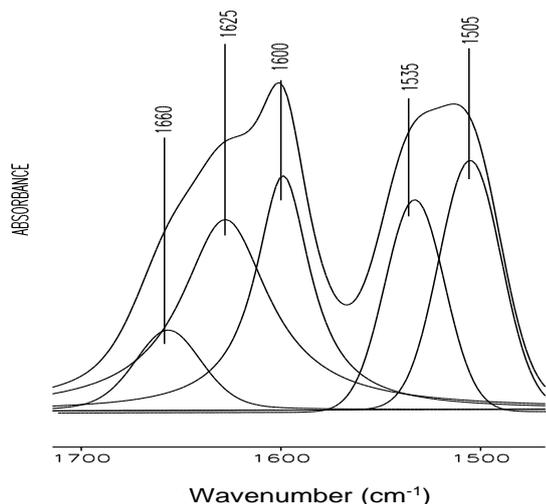


Fig. 4. Resolved IR-spectrum of NdL15 in the interval $1750-1450\text{ cm}^{-1}$

Additional attention was paid on the interval $3700-3000\text{ cm}^{-1}$ in the IR-spectrum. Following the synthetic procedure, the complexation is accompanied by deprotonation of the OH-groups, that's why no bands above 3200 cm^{-1} are to be expected. Nevertheless, overlapping bands at about 3600 cm^{-1} , $3450-3400\text{ cm}^{-1}$ and 3200 cm^{-1} are present in the IR interval mentioned (Fig. 5 (1)).

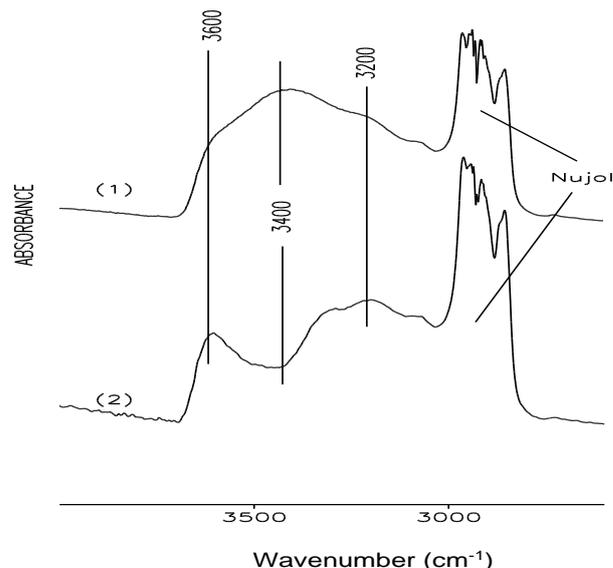


Fig. 5. Original (1) and reduced (2) IR-spectrum of NdL15 in the interval $3700-2650\text{ cm}^{-1}$

In order to precise the IR data from Fig. 5, decomposition/deconvolution of the spectral curve was made (Fig. 6). The doublet at 3624 cm^{-1} and 3577 cm^{-1} can be assigned to the presence of non-influenced OH-groups, while the bands at 3315 cm^{-1} and 3200 cm^{-1} to water molecule covalently bonded; it is unlikely to be due to strongly associated OH-bonds. The intensive broad band at 3445 cm^{-1} can be assigned for mechanically involved water. This is proved by the subtraction in the IR-spectrum of humidified KBr tablet, where the band is reduced and eliminated as shown in Fig. 3 (2), Fig. 5 (2).

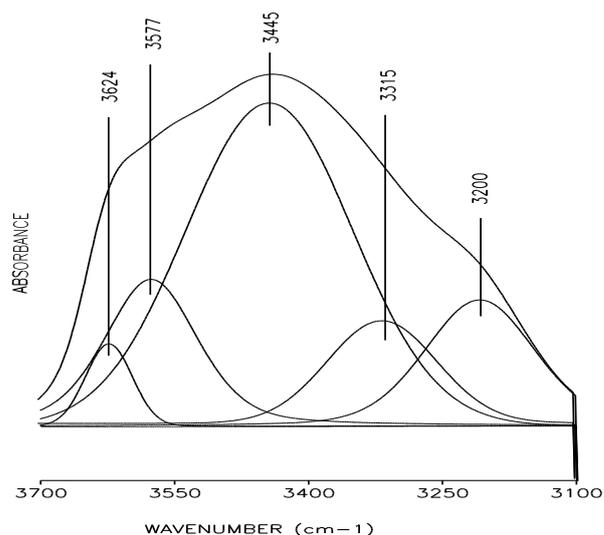


Fig. 6. Deconvoluted IR - spectral curve of the NdL15 in the area $3700 - 3100\text{ cm}^{-1}$

3.1.2. IR spectra of L11 and its corresponding complexes

Both complexes of L11, namely NdL11 and NdL11-AN2 are discussed below. In IR spectrum of NdL11 synthesized via deprotonation of the ligand changes were observed both for the frequencies for carbonyl and hydroxyl group of the coumarin ligand, as to be expected (Fig. 7). The position of the absorption maximum at the pure ligand is analogous to the one of L15. Here because of formation of very strong hydrogen bonds C=O-stretching vibration is anomalously decreased to 1665 cm^{-1} . The bands typical for the benzene rings at 1610 cm^{-1} and 1570 cm^{-1} (Fig. 7) are observed as well. In the spectrum of the complex the band for C=O group is lowered and observed at 1603 cm^{-1} . Changes were observed also for O-H groups; δ (COH) in the spectrum of the ligand at 1384 and 1323 cm^{-1} didn't appear in the complex. Multiplet band structure, similar to the one in IR spectrum of L15, is observed in the interval $3200 - 2650\text{ cm}^{-1}$. The multiplet is influenced by the complex formation of NdL11 so only two weak bands at 2935 and 2870 cm^{-1} can be seen (Fig. 7, red line); these two are missing in IR spectrum of NdL15. In spite of the fact that both complexes are result of the same synthetic procedure, in NdL11 the number of H_2O molecules is bigger i.e. 12, while in NdL15 they are 4, based on the elemental analysis. As long as there is OH-group for OH---O bonds in NdL11, the bands at 2935 and 2870 cm^{-1} in NdL11 could be considered as a result of H-bonding. As a comparison, $\text{TbL}\cdot 7.2\text{ H}_2\text{O}$ [10] does not show any bands in the IR spectrum interval of question because of lack of OH-group.

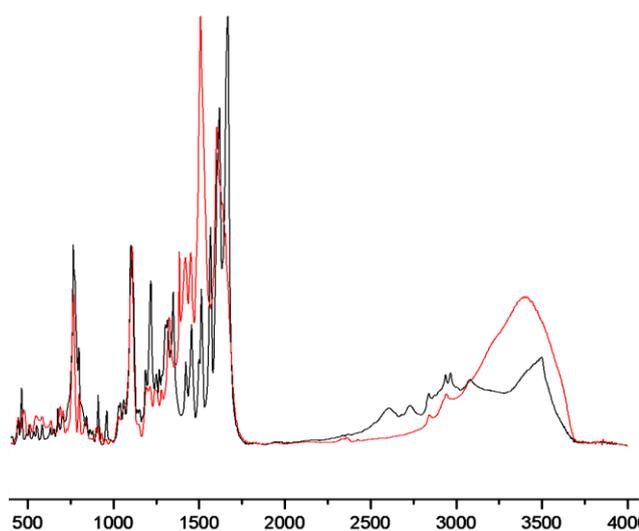


Fig. 7. Infrared spectrum $500\text{-}4000\text{ cm}^{-1}$ of L11 (black line) and of NdL11 (red line (color online))

Fig. 8 gives the IR spectra of L11 and NdL11-AN2 in the interval $1750\text{-}1250\text{ cm}^{-1}$. The comparison of those gives the following: In NdL11-AN2 as well as in NdL11 the band at 1640 cm^{-1} is missing and an intensive absorption maximum at 1500 cm^{-1} is revealing up. Apparently, in spite

of the difference in the synthetic route, the carbonylic group is participating in a similar way in the complexation.

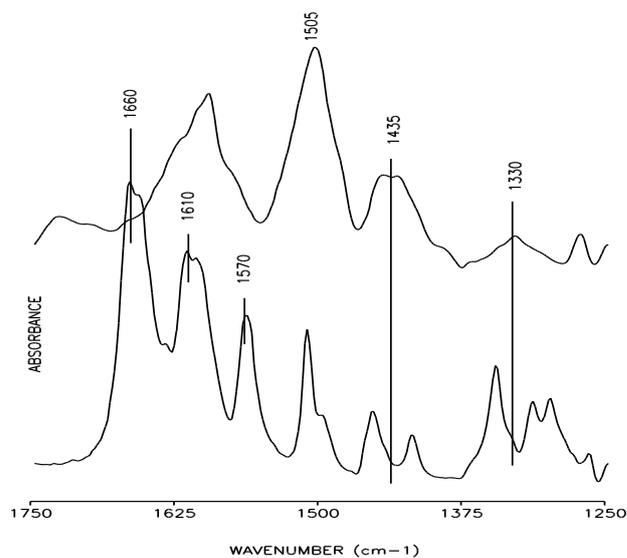


Fig. 8. Infrared spectrum $1750\text{-}1250\text{ cm}^{-1}$ of L11 (down) and of NdL11-AN2 (up)

The additional bands at 1435 cm^{-1} (ν_4) and 1330 cm^{-1} (ν_1) in the IR spectrum of NdL11-AN2 are due to the presence of nitrate groups from $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ used and they are assigned to asymmetric and symmetric stretching vibration of the nitrate anion. In the IR spectrum of $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ the respective values are 1465 cm^{-1} and 1315 cm^{-1} (Fig. 9). The shift of each of the two bands in the spectrum of the complex is a direct indication that NO_3 ion participates in complexation. The other bands marked on Fig. 9 correspond to deformational vibration of crystallization water (1635 cm^{-1}), to symmetric stretching vibration of the nitrate ion (1040 cm^{-1}), to its out-of-plane (815 cm^{-1}) and in-plane (745 cm^{-1}) deformational vibrations. From the spectrum of the complex, information regarding the possible bonding mode of the nitrate group can be obtained. The difference between the two frequencies is used as a criterion for differentiation between mono and bidentate chelating nitrates [18]. In that case $\Delta\nu = \nu_4 - \nu_1$ is about 105 cm^{-1} , moreover two weak peaks at 1705 cm^{-1} and 1718 cm^{-1} with a separation of 13 cm^{-1} appear in the combination mode region [19]. The observed separation of both frequencies (ν_4 and ν_1) and that of the combination mode indicate monodentate mode of coordination of the nitrate groups in the complex [18].

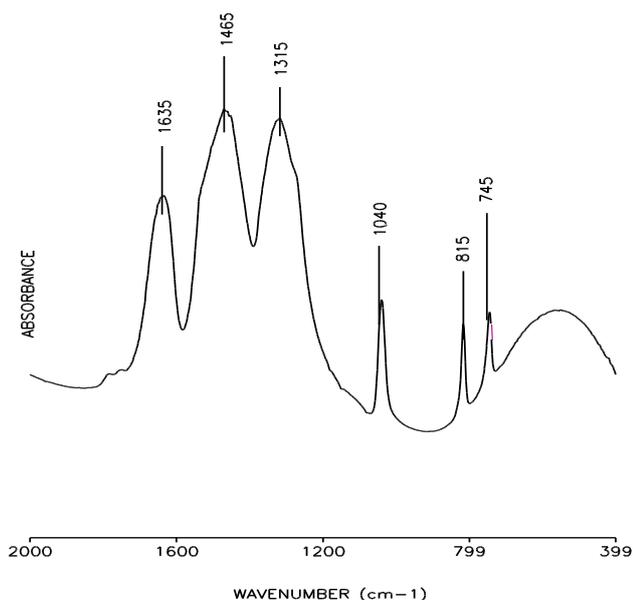


Fig. 9. IR spectrum of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in $2000\text{--}400\text{ cm}^{-1}$

3.2. Molecular structure of the complexes

As already mentioned no single crystals from the complexes were isolated. Thus, the probable molecular structure was interpreted based on the results from elemental analysis and IR spectroscopy.

For complexes of the type $\text{Ln}_2\text{L}_3 \cdot n\text{H}_2\text{O}$, where L is 3,3'-[(4-chlorophenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) and 3,3'-[(3,5-dimethoxy-4-hydroxyphenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) the possible structure proposed is equal to [13, 16]. The experimental results and also literature data gave as a reason to consider complexation through carbonylic and hydroxylic oxygen atoms, since these sites are most likely preferred for coordination. We should consider that in solid state the complex exists as polymeric structure. Preferably for Ln(III) ion high coordination number was observed in the binuclear monomer unit with the bis-coumarin ligands chelated in a tetradentate mode.

In the complex $[\text{NdL}_2(\text{NO}_3)_3] \cdot 2\text{CH}_3\text{CN}$, where L is 3,3'-[(3,5-dimethoxy-4-hydroxyphenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) the ligand acts as bidentate *via* its carbonyl oxygen atoms. The formed complex is mononuclear, as the Nd(III) ion is connected with two bis-coumarin molecules along with nitrate group acting in a monodentate mode. The monomeric structure of the mixed-ligand complex is proposed (Fig. 10).

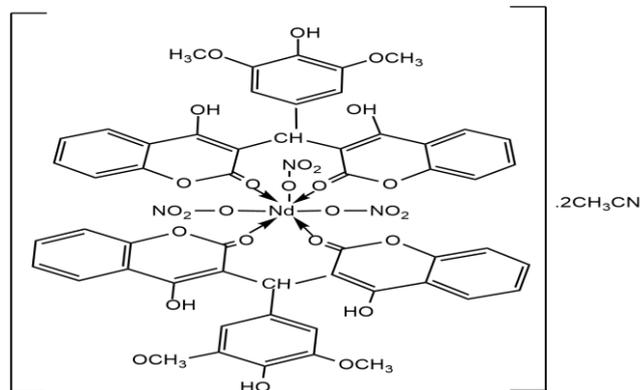


Fig. 10. Proposed molecular structure of the complex of Nd(III) with L15

3.3. Optical properties of the ligands and complexes

3.3.1. Excitation and emission spectra of the ligand L15 and its corresponding complexes

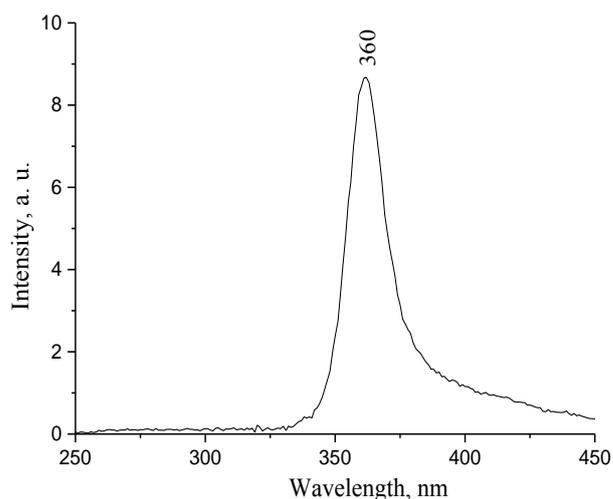


Fig. 11. Excitation spectrum of L15

The fluorescence spectra of the pointed ligand and its Tb(III) complexes were recorded at room temperature. Fig. 11 gives the excitation spectrum of the ligand, where a sharp excitation peak at 360 nm can be seen. In the emission spectrum [13] a broad band with maximum at 478 nm was detected. The bands observed are due to the $\pi\text{-}\pi^*$ transitions in chromophore system in the coumarin moiety. The large enough Stokes shifts helps to avoid an overlapping of the excitation and emission spectra what is within an agreement with the literature statements [20]. On the other side the broad emission band could easily influence some of the bands in Tb(III) emission spectra as can be seen below.

The excitation spectra of TbL15 in DMF-solution (Fig. 12 a) and in solid phase (Fig. 12 b) are presented below. The sharp band in the spectrum of the dissolved sample with maximum at 350 nm can be considered equal to the broad one with maximum at 343 nm of the powdered sample. The main excitation band in both spectra can be considered as consequence of already mentioned $\pi\text{-}\pi^*$ transitions of the

coumarin moiety in the complexes. Observed changes in both spectra were due to the impact of the solute. Probably the complex exhibit different environment when it is in solution and in solid state.

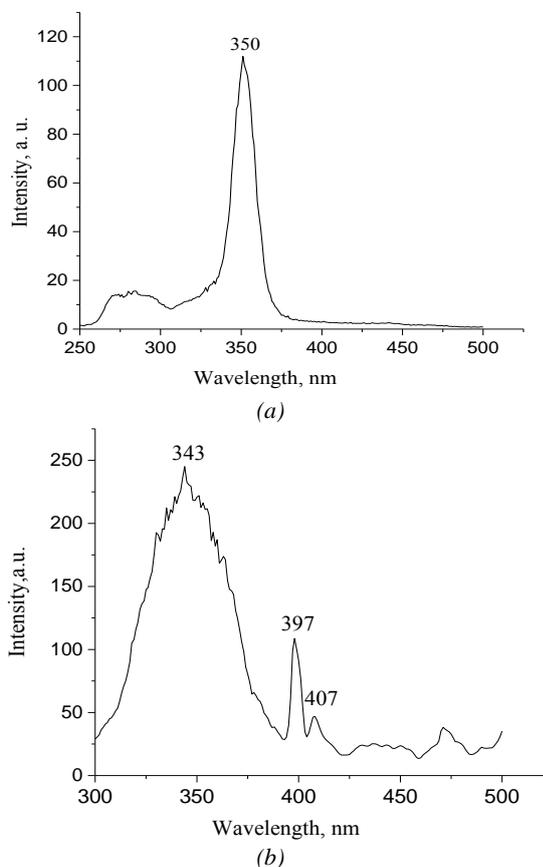


Fig.12. Excitation spectra of TbL15 in DMF-solution (a) and in solid phase (b)

After excitation of the sample of TbL15 with UV-light, green light emission was detected as can be seen in Fig. 13. The observed luminescence can be considered as a good proof for presence of Tb(III) ion in the complex. Evident from the picture of fluorescent microscope the morphology of the powder is presented from unequal and irregular shape of the particle agglomerations.

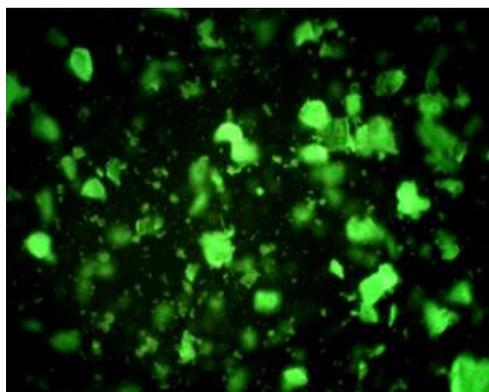


Fig. 13. Fluorescence of the powder sample of TbL15 complex, observed by fluorescent microscope (color online)

When excited at 360 nm typical for Tb(III) ion energy transitions in the emission spectra of complexes TbL15 [13] and TbL15-Et (Fig.14) were observed. The two complexes have similar emission spectra, considering similar environment around the central ion. Similar composition of the two complexes is suggested also from results of elemental analysis.

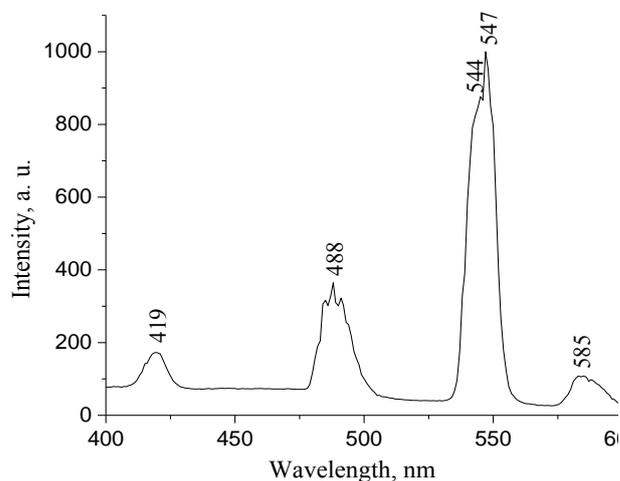


Fig. 14. Emission spectrum of TbL15-Et, excited at 360 nm

The bands correspond with the well-known $^5D_4 \rightarrow ^7F_j$ transitions ($j = 0-6$) from the lowest excited state 5D_4 to the highest ground state 7F_0 and next 7F_j ($j = 0-6$) of the ion. The maximum intensity of electric dipole transition ($^5D_4 \rightarrow ^7F_5$) indicated the highly polarizable chemical environment around the central metal ion, which controlled the green luminescent color of the complex. According to the literature [21], $^5D_4 \rightarrow ^7F_2$ transition has low intensity ($15485-15218 \text{ cm}^{-1}$), $^5D_4 \rightarrow ^7F_1$ - very low intensity (14975 cm^{-1}), and $^5D_4 \rightarrow ^7F_0$ (14690 cm^{-1}) transitions with the lowest intensity. In our complexes these transitions are difficult to be detected, considering their low symmetry and their X-ray amorphousity.

The Tb(III) emission at 544 nm may be assigned to a multiplet radiative transition denoted $^5D_4 \rightarrow ^7F_5$. According to [2] this emission arises from an intraconfigurational f-f transition which is retained even when terbium is present at concentration as low as 10^{-5} M . According to [22] the emission spectra of Tb(III) are dominated by mixed electric dipole/magnetic dipole transitions. Since, electric dipole transitions in lanthanoid ions are induced by the ligand field their probabilities are quite sensitive to the latter [23]. The water molecules in the Nd(III) and Tb(III) containing complexes form a ligand field with different strength. The presence of water molecules located in the inner coordination sphere of Tb(III) complexes obviously does not impact on their fluorescent properties.

It is not the situation with the analogous Nd(III) complexes also containing coordinated water molecules. For instance, in the case of NdL15 fluorescence was not register at irradiation with UV light [13]. So, a possible reason can be the quenching of the fluorescence by the water molecules which impact is stronger expressed on the

energetic levels of the Nd(III) ion, than on Tb(III) ion. According to [24] due to the larger energy gap between the lowest excited level and the highest ground state manifold, Tb(III) is not as sensitive to O-H vibrations as the other lanthanoids. It is known that both inner-sphere and outer-sphere water molecules create fluorescence quenching [21]. Excitation and emission spectra matched for Tb(III) complexes only, suggesting that the charge transfer from the ligand (in that case L15) to Nd(III) was not enough to sensitize the metal ion.

3.3.2. Excitation and emission spectra of the ligand L11 and its corresponding complex

The spectrum of ligand L11 is shown on Fig. 15, where excitation at 347 nm and emission at 395 nm can be detected. Considering the fact that the ligands used differ in the substitutes of the benzene ring, one can suggest an impact of those substitutes to the observed fluorescent properties. Significant difference is seen between the very sharp, narrow emission band of L11 (containing two methoxy groups, and a hydroxyl group) and the very broad one of L15, which have a chloro- group respectively. Differences have to be looked for in the other ligands spectra so to extract a sustainable conclusion.

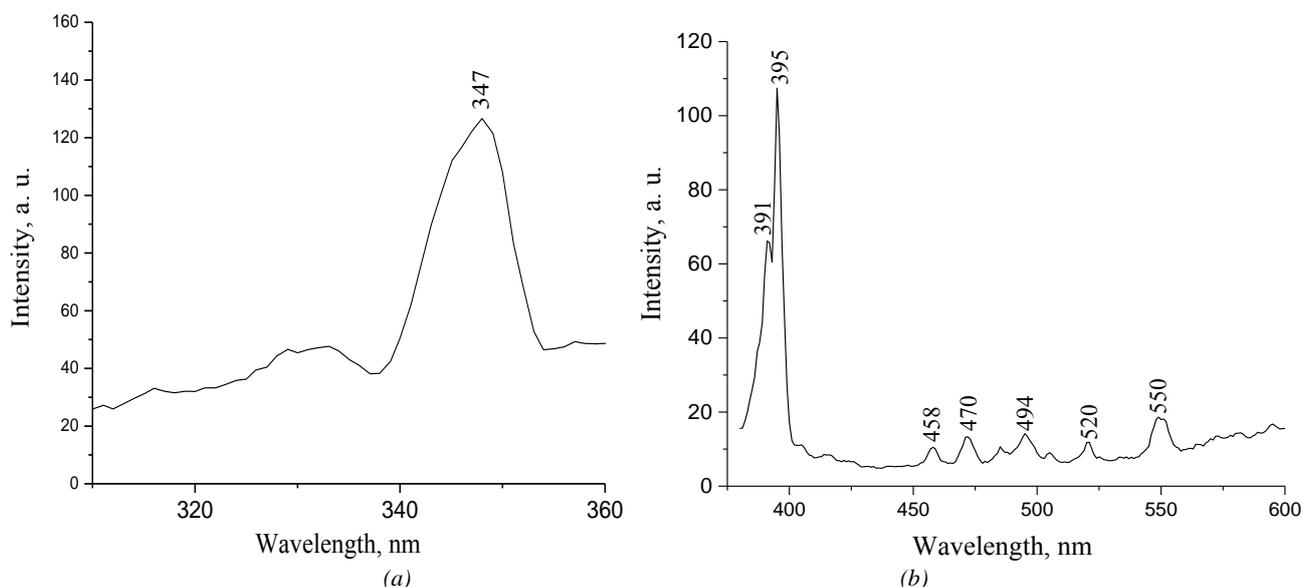


Fig. 15. Excitation (a) and emission (b) spectra of L11

Quenchers of the fluorescence can be not only O-H – vibrations but different molecular vibrations in the ligand that encapsulates the ion, in particular C–H, N–H are very capable quenchers [25]. So, we can consider that there are also C–H oscillators in our ligands. A confirmation for that is the fluorescence observed for the complex NdL11-AN2 (Fig. 16) which is obtained at synthesis from acetonitrile solution. The only water molecules are introduced in the synthetic solution by the $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salt, used as an initial Nd(III) source. The elemental analysis does not suggest water included in the complex but acetonitrile. Actually, the only registered transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ in the spectra with different intensity is the one responding to the very intensive band at 1050 nm. That band is within the range of telecommunication window [26], which makes the complex potential optical material. Bands with lower intensity at around 870 (${}^4\text{F}_{3/2} \rightarrow {}^4\text{F}_{9/2}$ transition) and 1350 nm (${}^4\text{F}_{3/2} \rightarrow {}^4\text{F}_{9/2}$ transition) are missing. The reason for that could be also the peculiarities of the NdL11-AN2 complex, namely its low symmetry and X-ray amorphous like those of Tb(III) complexes.

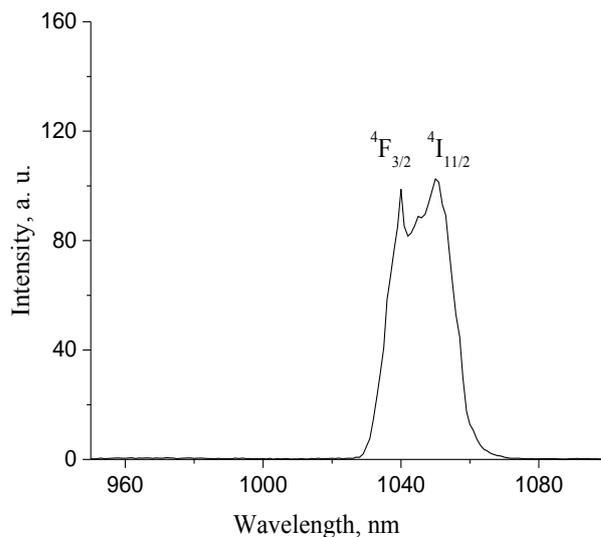


Fig. 16. Emission spectrum of NdL11-AN2

4. Conclusions

In the present study three different synthetic procedures were applied not used for the complexes preparation of Ln(III) with bis-coumarin derivatives as ligands. Polymeric and monomeric complexes of 3,3'-[(phenylmethylene)]bis(4-hydroxy-2H-1-benzopyran-2-one) derivatives with Tb(III) and Nd(III) were synthesized.

For the polymeric complexes of type $\text{Ln}_2\text{L}_3\cdot n\text{H}_2\text{O}$ ($\text{Ln}:\text{L}=1:1.5$) by spectral curve decomposition of IR-spectra the coordination ability of the carbonylic and hydroxylic oxygen atom of the ligand to Ln(III) was successfully confirmed as well as the presence of water molecules included in the inner coordination sphere.

By simple technique the chemically bonded water molecules were distinguished from the mechanically adsorbed water. The lanthanoid ions possess variety of coordination numbers, confirmed by the synthesis of complexes with a composition of $\text{Ln}_2\text{L}_3\cdot n\text{H}_2\text{O}$ and different number of water molecules ($n=2, 4, 12$). Considering the big size of the coumarin ligands, at $n=12$ a steric hindrance can be expected. The latter one can be evaluated only on the base of single crystals XRD data.

The acetonitrile aprotic solvent, used as media in the third synthetic route, determined the coordination of the coumarin ligand which occurred to be different than the one in water solution. In the aprotic solvent a second ligand, nitrate group, was coordinated to Ln(III) ion and by that a mixed-ligand complex was formed. For the complex of the type $[\text{NdL}_2(\text{NO}_3)_3]\cdot 2\text{CH}_3\text{CN}$ possible structure was proposed. Future experimental evidences based on XRD of single crystals can confirm that.

The optical properties of the complexes strongly depend on the energy transfer between the ion and the ligand. The fluorescence of Tb(III) and Nd(III) complexes experience a different impact by the presence of water molecules in the ion environment. A possible reason could be the O-H quenching as well as not sufficient energy transfer from the ligand to the emitting level of Nd(III) ion. More detailed investigations are needed to be carried on, in order to find out the reason for not observing fluorescence of Nd(III) ion in complexes of the type $\text{Ln}_2\text{L}_3\cdot n\text{H}_2\text{O}$. That means to determine the energy of the triplet state of the ligand in deprotonated form.

By synthetic procedures in water-free medium Nd(III) complexes without water molecules can be obtained so to preserve their fluorescence in the near-infrared region.

In spite of the fact that complexes of two out of 14 lanthanoid ions are investigated, the same structure for the complexes of the other Ln(III) can be presumed, taking into account the well-known similarities of these elements. This cannot be valid for the optical properties of the elements where the emitting levels of each Ln(III) should be considered.

The potential applications of the complexes synthesized can be seen in their fluorescence properties for example after immobilization in suitable matrices for fluorescent devices.

Acknowledgments

The financial support of the Bulgarian Fund for Scientific Investigation by Contract DO 02-129/08 is highly acknowledged.

References

- [1] T. Smirnova, N. Nevryuva, S. Shtykov, V. Kochubei, D. Zhemerichkin, *J. Analyt. Chem.* **64**, 1114 (2009).
- [2] J. Kido, Y. Okamoto. *Chem. Rev.* **102**, 2357 (2002).
- [3] F. Prendergaet, J. Lu, P. Callahan, *J. of Biological Chem.* **258** (7), 4075 (1982).
- [4] S. Quici, M. Cavazzini, G. Marzanni, G. Accorsi, N. Armaroli, B. Ventura, F. Barigelletti. *Inorg. Chem.* **44**, 529 (2005).
- [5] A. Vogler, H. Kunkele, *Inorganica Chimica Acta* **359**, 4130 (2006).
- [6] S. Faulkner, S. J. A. Pope, B. P. Burton-Pye. *Applied Spectroscopy Reviews* **40**, 1 (2007).
- [7] N. S. Kariaka, V. A. Trush, P. Gawryszewska, V. V. Dyakonenko, S. V. Shishkina, T. Yu. Sliva, V. M. Amirkhanov, *Journal of Luminescence* **178**, 392 (2016).
- [8] I. Kostova, G. Momekov, P. Stancheva. *Metal Based Drugs* **2007**, 1 (2007).
- [9] I. Georgieva, I. Kostova, N. Trendafilova, V. Rastogi, W. Kiefer. *J. Mol. Spectrosc.* **979**, 115 (2010).
- [10] D. Elenkova, R. Monov, A. Tadjer, I. Manolov, M. Milanova. *J. Mol. Structure* **1106**, 491 (2015).
- [11] D. Elenkova, M. Getsova, J. Zaharieva, I. Manolov, M. Milanova. *Centr. Eur. J. Chem.* **11**, 1032 (2013).
- [12] D. Elenkova, B. Morgenstern, I. Manolov, M. Milanova. *Acta Chim. Slov.* **61**, 718 (2014).
- [13] M. Milanova, J. Zaharieva, I. Manolov, M. Getsova, D. Todorovsky, *J. Rare Earths (Spec. Issue)* **28**, 66 (2010).
- [14] I. Manolov, C. Maichle-Moessmer, *Eur. J. Med. Chem.* **41** (7), 882 (2006).
- [15] D. Elenkova, Ph D Thesis (2015).
- [16] Tz. Mihaylov, N. Trendafilova, I. Georgieva, *J. Mol. Modeling* **14**, 353 (2008).
- [17] R. S. Keri, K. M. Hosamani, R. V. Shingalapur, M. H. Hugar, *Eur. J. Med. Chem.* **45**, 2597 (2010).
- [18] K. Nakamoto, *Infrared spectra of Inorganic and Coordination Compounds*, Wiley and Sons, (1978).
- [19] I. S. Ahuja, *IJCA*, 21A 936 (1982).
- [20] M. Wertz, *Science Progress* **88**(2), 101 (2005).
- [21] S. A. Cotton, *Lanthanide and Actinide Chemistry*, Wiley and Sons, Uppingham 1 (2006).
- [22] H. Katerinopoulos, *Curr. Pharm. Des.* **10**(30), 3835 (2004).
- [23] I. Hemmila, V. Laitala. *J. Fluorescence*, **15** (4), 529 (2005).
- [24] N. Sabbatini, M. Guardigli. *Coord. Chem. Rev.* **123**, 201 (1993).

[25] Y. Hasegawa, T. Ohkubo, K. Sogabe,
Y. Kawamura, Y. Wada, N. Nakashima, S. Yanagida,
Angew. Chem. Int. Ed. **39**, 357 (2000).

[26] J.-C. G. Bünzli, S. Eliseeva, J. Rare Earths **28**,
824 (2010).

*Corresponding author: nhvk@chem.uni-sofia.bg